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Section A. The Interaction of Perfluorobutadiene with Iron and
Cobalt Carbonyls

By R.L. HUNT, D.M. ROUNDHILL, and G. WILKINSON.

Apart from a quotation¹ of unpublished work by Chatt and Guy to the effect that perfluorobutadiene forms an unstable complex with platinum, the only other studies involving transition metals is a recent mention² of its interaction with certain carbonylate anions.

Interaction with pentacarbonyliron

Perfluorobutadiene and pentacarbonyliron in petroleum solution interact under mercury-sensitised ultra-violet radiation to yield a yellow solid, which, on vacuum sublimation yields transparent colourless to greenish-yellow crystals. We have been unable to promote this reaction thermally, but dodecacarbonyltririron in petroleum reacts with perfluorobutadiene at ca. 120° for 12 hours to give, after purification by sublimation, a similar product of somewhat lower melting point. This substance appears to be a mixture of the first complex with another (doubtless an isomer, as noted below) so similar to it that we have been unable to separate them by chromatography, the difficulty in part being due to decomposition on the columns.

The first substance, which melts sharply at 61 - 61.5° analyses as $C_4F_6Fe(CO)_4$ and has the correct molecular weight. The i.r. shows four terminal carbon monoxide stretching frequencies, bands due to

C-F groups and, in addition, a single sharp band at 1754 cm^{-1} which is assigned as a C=C stretching frequency.

The ^{19}F n.m.r. spectrum has two peaks at -4.0 and $+71.9$ p.p.m. relative to benzotrifluoride reference the area ratios being respectively 2:1. The low field peak is complex but compatible with an A_2X_4 system having a main doublet separation 6.8 c/sec. and is in a position typical for a $-\text{CF}_2-$ group σ -bonded to a metal.³ The high field line shows also complicated and incompletely resolved splittings but the line position is consistent for that for olefinic fluorine groups. The only structure accommodating these facts is I which is hence very similar to the first known complex of this type which had a saturated fluorocarbon ring.³ X-ray crystallographic studies⁴ have confirmed this structure. The n.m.r. spectrum of the mixture referred to above suggests that the second component is an isomer with the double bond in the 2,3 position.

Interaction with octacarbonyldicobalt

The thermal interaction of octacarbonyldicobalt and perfluorobutadiene yields two products, one a non-volatile red substance which cannot be crystallised and which we have been unable to characterise, the other a material which can be readily purified by vacuum sublimation or crystallisation from solvents as large yellow crystals. The compound analyses as $\text{C}_4\text{F}_6\text{Co}_2(\text{CO})_6$ and the molecular weight is also correct. The mass spectrum shows the highest mass at 448 although this value is somewhat unprecise, with

peaks at 420, 392, 364, 335, 308 and 280. Although the successive loss of six carbon monoxide molecules is thus evident, there is no evidence for a species in which only the fluorocarbon has been lost; this is consistent with the strong binding of fluoroolefins and with other similar data.³ The complex is a non-conductor in nitrobenzene; it is unaffected by air in the solid state or in solution, by bromine at 85°, by iodine at 80°, strong acids, bases, or molten diphenylacetylene. With carbon monoxide at 150°/150 atm., partial conversion to octacarbonyldicobalt occurs.

The i.r. spectrum in solution shows three terminal carbonyl frequencies, peaks assignable to C-F but no bands due to bridging carbonyl or to C=C groups.

The ¹⁹F n.m.r. spectrum has two peaks of relative area 1:2 at +26.2 and +36.7 p.p.m. relative to benzotrifluoride. The high field line is a sharp doublet with separation 16.5 c/sec., but the low field line is unusually poorly defined and broad (75 c/sec.). These resonance positions are not consistent with σ -bonding of a fluoroalkyl group and the structure best consistent with the evidence is one involving a coordinated bridging perfluorobutadiene and a cobalt-cobalt bond (II). The extremely large unit cell found for this complex⁴ has made the X-ray structure determination very difficult, but the metal-metal distance does appear to be sufficiently short to satisfy the criterion for metal-metal bonding. This is in any case required by the observed diamagnetism of the complex.

Whilst attempts to substitute either the carbonyl or fluoroolefin ligands have failed, the cobalt-cobalt bond can be opened by additional ligand coordination to yield paramagnetic complexes which evidently have the structure III ($L = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{n-Bu}_3\text{P}$). Thus on refluxing $\text{C}_4\text{F}_6\text{Co}_2(\text{CO})_6$ with triphenylphosphine in petroleum, a very sparingly soluble adduct is obtained, which analyses as $\text{C}_4\text{F}_6\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$. This complex is paramagnetic with $\mu_{\text{eff}} = 2.0$ B.M. (1.4 B.M.) per metal atom at 298° ; over a temperature range, some deviation from the Curie-Weiss law is observed. The electron spin resonance spectra of the solid at 78°K and 295°K are almost identical and show three, not too well resolved lines, $g = 1.95, 2.67, 2.95$. The magnetic data is hence consistent with an unpaired electron on each cobalt atom but with some interaction probably due to the high magnetic concentration.

The comparable triphenylarsine complex is readily soluble in organic solvents such as chloroform, acetone and benzene although sparingly soluble in petroleum. This complex is also paramagnetic, $\mu_{\text{eff}} = 2.6$ B.M. at 292° ; the e.s.r. spectrum shows only a broad band centred at $g = 2.35$.

Experimental

Microanalyses and molecular weights (Mechrolab osmometer, 37°) by the Microanalytical Laboratory, Imperial College, and Dr. A. Bernhardt, Mülheim. I.r. spectra were recorded using a Grubb-Parsons Spectromaster grating instrument, n.m.r. spectra using a Varian V 4311 at 56.45 Mc/sec. (benzotrifluoride internal reference) and

e.s.r. spectra using a Varian V-4502--15. Mass spectra were taken using an MS-9 spectrometer. Melting points via Kofler hot-stage, uncorrected. Perfluorobutadiene was from the Peninsular Chemicals Company.

Interaction of perfluorobutadiene and pentacarbonyliron

An excess of C_4F_6 (2 ml.) and $Fe(CO)_5$ (1.5 ml.) in a sealed glass tube containing a little mercury, was irradiated with ultra-violet light for 24 hours. After removal of liquid in vacuum, the residue was crystallised from petroleum (b.p. 30 - 40°). The solid was then sublimed in vacuum from room temperature to a water-cooled probe to give the pure complex. Yield, ca. 100 mg., m.p. 61 - 61.5°. [Found: C, 29.0; F, 34.3; Fe, 17.0. \underline{M} , 325 (benzene). $C_8F_6FeO_4$ requires C, 29.1; F, 34.5; Fe, 16.9%. \underline{M} , 330.] I.R., ν_{max} (cyclohexane): 2153s, 2097s, 2092s, 2076s, 1752s, 1344m, 1310s, 1287sh, 1122s, 1090m, 1059m, 977s, 928s, 815m.

Interaction of perfluorobutadiene and octacarbonyldicobalt

An excess of C_4F_6 (3.5 ml.) and $Co_2(CO)_8$ (4 g.) in a thick-walled glass tube were heated at 100° for 24 hours. After opening and removal of excess C_4F_6 , the residue was extracted with petroleum (b.p. 40 - 60°) to leave a red residue. The solution was evaporated and the residue sublimed in vacuum at 60° to a water-cooled probe. Two crystallisations from petroleum (b.p. 30 - 40°) produced yellow needles of the complex. Yield, ca. 4 g., m.p. 85 - 85.5°. [Found: C, 27.1; Co, 26.3; F, 25.4. \underline{M} , 460 (benzene). $C_{10}Co_2F_6O_6$ requires C, 26.8; Co, 26.4; F, 25.4%. \underline{M} , 448.] I.R., ν_{max} (cyclohexane):

2132s, 2096s, 2079s, 1284m, 1244m, 1199s, 1100s, 994s, 888m, 730s, 665s.

Bis(triphenylphosphine)perfluorobutadiene hexacarbonyldicobalt

Perfluorobutadiene hexacarbonyldicobalt (0.2 g.; 1 equiv.) and triphenylphosphine (0.24 g.; 2 equiv.) in petroleum (20 ml., b.p. 60 - 80° were refluxed 2 hours and the yellow-orange precipitate of the complex then collected and washed with petroleum and acetone. Yield, quantitative; m.p., 146-150°. [Found: C, 56.6; H, 3.4; F, 12.5. $C_{46}H_{30}Co_2F_6O_6P_2$ requires C, 56.8; H, 3.1; F, 11.7%.] I.r., ν_{max} (nujol mull): 2073s, 2048s, 2024s, 2018s, 1236s, 1186s, 1164m, 1098m, 1088m, 1070m, 1042m, 1000m, 977m, 969s, 880s, 715s, 696s. The magnetic moment (from susceptibilities by the Gouy method, corrected for diamagnetism of ligands), μ_{eff} in B.M. °K: 2.0, 297°; 1.9, 254°; 1.8, 204°; 1.6, 155°; 1.4, 113°.

Bis(tri-*n*-butylphosphine)perfluorobutadienehexacarbonyldicobalt

In a similar way using stoichiometric quantities with tri-*n*-butylphosphine to yield an orange tar after removal of petroleum. This material was dissolved in methanol and cooled to -40° to give orange crystals of the complex which were collected and dried in vacuum. Yield, ca. 70%, m.p. 77.5 - 78°. [Found: C, 48.0; H, 6.6; Co, 14.0; F, 13.7. $C_{34}H_{54}Co_2F_6O_6P_2$ requires C, 47.9; H, 6.3; Co, 13.9; F, 13.4%.] I.r., ν_{max} (cyclohexane): 2058s, 2027s, 2008s, 1993m, 1381s, 1274s, 1230s, 1186s, 1092s, 1071s, 1053s, 977s, 882s, 775m, 712s.

Bis(triphenylarsine)perfluorobutadienehexacarbonyldicobalt

As for the Ph_3P complex to give the yellow complex essentially quantitatively. m.p., 110° with decomp. [Found: C, 52.2; H, 2.9; F, 10.8. \underline{M} , 1080 (CHCl_3). $\text{C}_{46}\text{H}_{30}\text{As}_2\text{Co}_2\text{F}_6\text{O}_6$ requires C, 52.1; H, 2.8; F, 10.8%. \underline{M} , 1060.] I.r. max (CH_2Cl_2): 2110m, 2045vs, 2018vs, 1931s, 1709w, 1597w, 1399m, 1220s, 1183s, 1157sh, 1073s, 1050ms, 977s, 878s.

Section B. Complexes derived from perfluorobut-2-ene and
tetrakis(trifluoromethyl)cyclopentadienone ("dixone")

By D.M. ROUNDHILL and G. WILKINSON.

Perfluorobutene-2 and tris(triphenylphosphine)platinum afford the complex which can be formulated $\text{Pt}(\text{PPh}_3)_2\text{C}_4\text{F}_8$. From published work on platinum fluorocarbon complexes one would expect this new complex to have the structure IV, and much evidence supports such a structure. Molecular weight data indicates the molecule to be monomeric, and the infrared (i.r.) spectrum shows bands due to C-F bonds, and also the absence of any bands which could be due to a carbon-carbon double bond. The n.m.r. spectrum shows two peaks centred at 2.5 and 140 p.p.m. upfield of the standard, benzotrifluoride. The relative areas of the two peaks are in the ratio 3:1. It is surprising however that it is the lowfield peak which is the one due to the $-\text{CF}_3$ group, since one expects these low chemical shifts to be due to a fluorine nucleus attached to a carbon atom in the 1 position with respect to the metal atom.

The problem has been further investigated by preparing the corresponding palladium in a similar stoichiometry $\text{Pd}(\text{PPh}_3)_2\text{C}_4\text{F}_8$, and again the i.r. spectrum indicates the presence of C-F bonds and the absence of a carbon-carbon double bond. The n.m.r. spectrum is again very similar consisting of two peaks centred at 4.0 ($-\text{CF}_3$) and 133 (CF) p.p.m. upfield relative to benzotrifluoride, although

since palladium has zero nuclear spin the spectrum is rather more simple than that for the platinum complex. Bis(triphenylarsine) platinum perfluorobutene-2 has also been synthesised as colourless crystals (m.p. 198-200°) and the i.r. spectrum shows the expected features. Although the n.m.r. spectrum has not been obtained, it should be very interesting since from the n.m.r. spectra of these three complexes it should be possible to unambiguously assign spin coupling constants due to $^{195}\text{Pt-F}$, $^{31}\text{P-F}$, and F-F coupling.

At present the best possible structure which can be given to these complexes is the one depicted in Fig. I, but the reversal of the expected position for the CF and -CF_2 fluorine resonances in the n.m.r. spectra has not yet been explained.

Perfluorobutene-2 has also been found to react with dicobalt octacarbonyl when the mixture is heated for several hours in a stainless steel bomb at 150°. The product, obtained in good yield, is a volatile waxy red solid. Analytical data has been obtained but is not very useful for structure determination because of the several possible formulae which have the same theoretical carbon content; also the molecular weight data which has been obtained is of little use. The mass spectrum of the complex shows only one really strong peak, which is at mass number 91 and which has not been identified, but the spectrum also shows a moderately strong peak at the highest position representing a fragment of mass 371. Although it is only speculative this could be due to a species having the structure $\text{Co(CO)}_4\text{C}_4\text{F}_8$, but at present such a

formulation could not be taken as proven.

When this waxy red complex is refluxed with excess triphenylphosphine in petroleum ether ($60-80^{\circ}$), the solution becomes darker, and on allowing the solution to cool to room temperature one obtains large ruby coloured crystals (m.p. $105-113^{\circ}$). Some analytical data has been obtained, which is in partial agreement with the formulation of the complex as monomeric in cobalt, but further analytical data would be necessary before a definite formula could be proposed.

Each complex shows i.r. bands due to carbon-fluorine bonds, and also 4 bands due to non-bridging metal carbonyl groups.

In addition to this work on perfluorobutene-2, a rather cursory study has been made of the chemistry of tetrakis(trifluoromethyl)cyclopentadienone, both in its reactions with other purely organic compounds, and in its reactions with transition metal complexes.

In general the compound is very reactive, and a yellow solution of it in dichloromethane is almost instantaneously decolourised by a dichloromethane solution of triphenylphosphine. The product obtained is insoluble in alcohol and colourless crystals (m.p. $219-224^{\circ}$) have been obtained. The analytical data indicates that the complex can be formulated as a 1:1 complex of the two reactants, namely $\text{PPh}_3\text{C}_9\text{F}_{12}\text{O}$. It is not certain how the two entities are bonded together, but it is of interest that the i.r. spectrum does not show any absorption bands at 1761 and 1718 cm.^{-1} ,

which have been ascribed to the ketonic carbonyl stretch, nor at 1684 cm.^{-1} which has been ascribed to the carbon-carbon double bond, in the original dienone. The dienone has also been found to react with other phosphines and also with amines.

The compound has also been shaken at room temperature with both triphenylarsine and carbon disulphide, but there is no reaction.

The dienone will react at room temperature with tris(triphenylphosphine)platinum(0) to give a complex which can be obtained from alcohol as colourless crystals. Analytical data shows the complex to have the formula $\text{Pt}(\text{PPh}_3)_2\text{C}_9\text{F}_{12}\text{O}$, and as in the other reaction products, the i.r. spectrum showed the absence of the bands at 1761 , 1718 and 1684 cm.^{-1} . A product has also been obtained from the facile interaction of the dienone with tris(triphenylphosphine)rhodium(I) chloride. The complex can be obtained as pale yellow crystals from alcohol, an i.r. spectrum showing the presence of C-F bonds.

Experimental

Bis(triphenylphosphine)perfluorobutene-2 platinum(0)

Tris(triphenylphosphine)platinum(0) and excess perfluorobutene-2 were sealed in vacuo in a thick-walled glass tube along with dichloromethane as solvent. The tube was shaken overnight, opened, and the excess perfluorobutene-2 removed. The remaining solution was transferred to a flask and boiled. To the boiling solution methanol was added until crystals appeared. After allowing

to cool the colourless crystals were filtered off and dried in vacuo (m.p. 229-231°). [Found: C, 52.4; H, 3.89; F, 18.3; \underline{M} (CHCl₃), 849. C₄₀H₃₀F₈P₂Pt requires C, 52.3; H, 3.3; F, 16.5; \underline{M} , 919.] ν_{\max} (saturated solution in CCl₄): 1477w, 1435m, 1370w, 1272s, 1180sh, 1172s, 1154s, 1096m, 1041m.

Bis(triphenylphosphine)perfluorobutene-2 palladium(0)

This complex was prepared in an analogous manner using tris(triphenylphosphine)palladium(0) and perfluorobutene-2. The complex was again obtained as colourless crystals. [Found: C, 57.3; H, 3.7. C₄₀H₃₀F₈P₂Pd requires C, 57.7; H, 3.6.] ν_{\max} (solution in CS₂): 1389w, 1290sh, 1276s, 1261s, 1227s, 1181, 1174s, 1145s, 1093s, 1050m, 1025m, 740s, 692s.

Bis(triphenylarsine)perfluorobutene-2 platinum(0)

Again an analogous method of preparation was used to give this complex as colourless crystals (m.p. 198-200°) using tris(triphenylarsine)platinum(0) and perfluorobutene-2. [Found: C, 48.5; H, 3.5; \underline{M} (CHCl₃), 741. C₄₀H₃₀F₈As₂Pt requires C, 47.7; H, 3.0; \underline{M} , 1008.] ν_{\max} (solution in CS₂): 1379w, 1269s, 1176sh, 1170s, 1148s, 1125s, 1104m, 1076m, 1021m, 999m, 781s, 691s.

Cobalt carbonyl perfluorobutene-2

An excess of perfluorobutene-2 was condensed onto dicobalt octacarbonyl in a stainless steel bomb. After the bomb had been heated at 150°C for 12 hours, the excess perfluorobutene-2 was removed, and the contents of the bomb washed out with petroleum ether (30/40°). Sublimation in vacuo of the product on to a water-

cooled probe gave deep red waxy crystals. Recrystallisation was carried out at -40°C from a small quantity of light petroleum (30/40 $^{\circ}$).

[Found: C, 24.7; H, 0.0; $\underline{M}(\text{CHCl}_3)$, 750; \underline{M} (mass spectrum), 371.]

ν_{max} (solution in CCl_4): 2133vs, 2088vs, 2058vs, 2024mw, 1600s, 1282vs, 1190vs, 1144vs, 956m, 932m, 682vs, 661s.

Cobalt carbonyl triphenylphosphine perfluorobutene-2

When cobalt carbonyl perfluorobutene-2 is refluxed for 3 hours with excess triphenylphosphine in petroleum ether (60/80) the solution becomes darker in colour. On cooling one obtains small ruby-coloured needle-like crystals (m.p. 105-113 $^{\circ}$). These crystals were filtered off and dried in vacuo. [Found: C, 49.5; H, 3.7;

$\underline{M}(\text{CHCl}_3)$, 677. $\text{C}_{26}\text{H}_{15}\text{F}_9\text{O}_4\text{PCo}$ requires C, 49.3; H, 2.4; \underline{M} , 633.]

ν_{max} (solution in CCl_4): 2096vs, 2049vs, 2024vs, 2000vs, 1457m, 1433s, 1302w, 1263s, 1183vs, 1122vs, 1092s, 1027w, 692s, 677s.

Tetrakis(trifluoromethyl)cyclopentadienone triphenylphosphine

Tetrakis(trifluoromethyl)cyclopentadienone (0.12 g.) was dissolved in dichloromethane, and triphenylphosphine (0.12 g.; 1.3 mole), dissolved in dichloromethane, ^{added.} The yellow colour of the solution soon disappeared, but the flask was shaken for a further hour. The solvent was then removed in vacuo, and the remaining solid recrystallised from chloroform/ethanol to give colourless crystals (m.p. 219-224 $^{\circ}$). [Found: C, 52.2; H, 3.6; F, 36.8; $\underline{M}(\text{CHCl}_3)$, 619. $\text{C}_{27}\text{H}_{15}\text{F}_{12}\text{PO}$ requires C, 52.8; H, 2.5; F, 37.1; \underline{M} , 614.] ν_{max} (nujol mull): 1580m, 1520m, 1280s, 1220s, 1190s, 1120s, 1020m, 1000w, 920s, 750ms, 735s.

Tetrakis(trifluoromethyl)cyclopentadienone bis(triphenylphosphine) platinum(0)

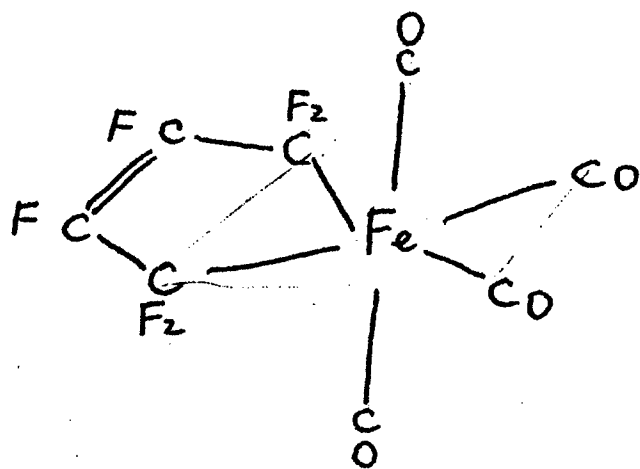
Tetrakis(trifluoromethyl)cyclopentadienone and tris(triphenylphosphine)platinum(0) were dissolved in dichloromethane and the solution mixed. The two compounds reacted to give a pale brown solution. The solution was boiled and methanol was added to the boiling solution until colourless crystals were formed. These were filtered off and dried in vacuo. [Found: C, 50.2; H, 4.4. $C_{45}H_{30}F_{12}P_2O$ Pt requires C, 50.4; H, 2.8.] μ_{\max} (nujol mull): 1305s, 1278s, 1215s, 1120s (C-F bands).

Tetrakis(trifluoromethyl)cyclopentadienone bis(triphenylphosphine) rhodium(I) chloride

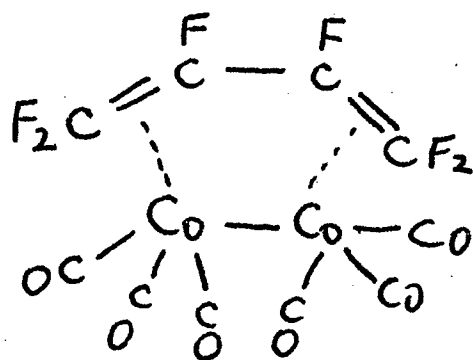
Using the same experimental procedure as for the previous platinum complex, pale yellow crystals of this rhodium complex were obtained. [Found: C, 56.9; H, 4.5; $\underline{M}(\text{CHCl}_3)$, 697. $C_{45}H_{30}F_{12}ClORh$ requires C, 56.7; H, 3.2; \underline{M} , 953.] μ_{\max} (nujol mull): 1580m, 1280s, 1210s, 1160mw, 1120s, 1040s, 1000s, 940s.

References

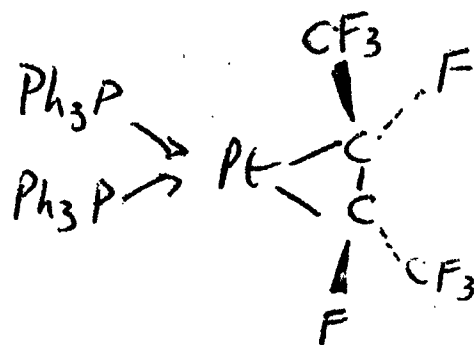
1. R.G. Guy and B.L. Shaw, Adv. Inorg. Chem. Radiochem., 1962, 4, 99.
2. M. Green, N. Mayne, and F.G.A. Stone, Chem. Comm., 1966, 755.
3. H.H. Hoehn, L. Pratt, K.F. Watterson, and G. Wilkinson, J. Chem. Soc., 1961, 2738.
4. R. Mason, Sheffield University, personal communication.



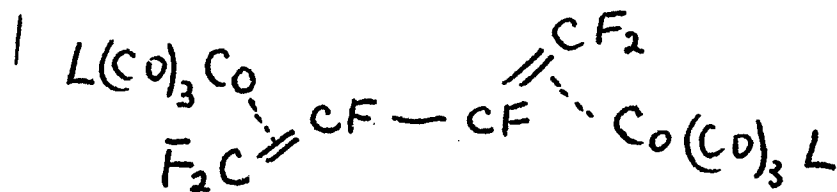
I



II



IV



III